Impurity-induced frustration in correlated oxides

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(Dated: March 24, 2009)

Using the example of Zn-doped La_2CuO_4, we demonstrate that a spinless impurity doped into a non-frustrated antiferromagnet can induce substantial frustrating interactions among the spins surrounding it. This counterintuitive result is the key to resolving discrepancies between experimental data and earlier theories. Analytic and quantum Monte Carlo studies of the impurity-induced frustration are in a close accord with each other and experiments. The mechanism proposed here should be common to other correlated oxides as well.

Impurities are known to be an effective tool to locally perturb quantum systems, thereby revealing important information about their microscopic interactions and correlations [1]. A well studied example of a strongly correlated quantum system in which effects of such impurity doping can be investigated is La_2CuO_4—one of the most important cuprate superconductor parent compounds. In its pristine form, this material is a two-dimensional (2D) spin-$\frac{1}{2}$ Heisenberg antiferromagnet (AF) [2]. It is believed that the substitution of Cu^{2+} ($S = \frac{1}{2}$) ions by spinless Zn^{2+} represents a good realization of the site-diluted Heisenberg hamiltonian [3, 4, 5, 6]. In this Letter, we demonstrate that there exists a significant *qualitative* correction to the dilution picture. Impurities can induce substantial *frustrating interactions* between nearby spins. Not only does this effect explain discrepancies between experimental data and the dilution-only theories for $La_2Cu_{1-x}Zn_xO_4$, but it may also be important for a variety of other phenomena in diluted magnets and doped Mott insulators. Our mechanism for such an effect should be common to many charge-transfer insulators, including oxides of transition metals.

We propose that the presence of extra degrees of freedom due to oxygen orbitals necessarily results in frustrating terms in the corresponding low-energy spin hamiltonian of the Zn-doped system, which are absent in the dilution-only models. Utilizing quantum Monte Carlo (QMC) and analytic T-matrix approaches, we calculate the doping dependence of the staggered magnetization for such a low-energy model. We show that this model, with the parameters appropriate for the CuO_2 planes given by a three-band Hubbard model calculation, naturally explains experimental data.

Experiments and theories.—Comprehensive studies of the problem of La_2CuO_4 diluted by spinless Zn impurities have been performed using neutron scattering, magnetometry, and NMR (NQR) on the experimental side [3, 4], and QMC and T-matrix approaches of the diluted Heisenberg model on the theoretical side [5, 6, 7]. These studies allow for extensive cross-checks. The unbiased QMC data agree with the T-matrix results closely up to $x \simeq 15\%$, supporting the validity of the latter in the low-doping regime [5, 6]. However, there are serious discrepancies between theoretical and experimen-

tal results. Fig. 1 shows the average magnetic moment M per Cu site versus the Zn doping fraction x. The experimental data are always below the theoretical curves. The slope

$$R(x) = \frac{1}{x}\left(1 - \frac{M(x)}{M(0)}\right),\qquad(1)$$

at small x represents the rate at which the order parameter M is suppressed by individual impurities due to enhanced quantum fluctuations. The inset of Fig. 1 shows a large discrepancy—a factor of approximately two—between the theoretical and experimental results. This indicates that the dilution-only theory significantly underestimates the impact of the impurity on the quantum spin background.

One might attempt to explain the disagreement by suggesting that longer-range (J_2, J_3, etc.), and ring-exchange interactions should be included in the model for the undoped CuO_2 plane. Such terms are generally present in the low-energy spin models derived from the Hubbard model [9], and they do lead
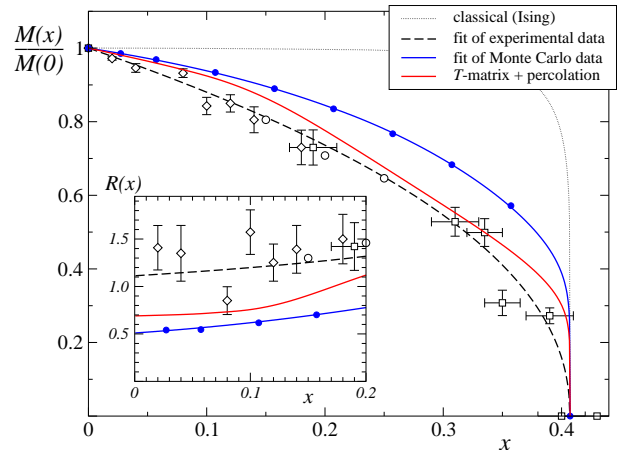

FIG. 1: (Color online). The on-site magnetic moment $M(x)$ per Cu normalized by its undoped value vs Zn doping x. Symbols show neutron scattering [3] (squares) and NQR [4] (diamonds and circles) data, with dashed lines their best fits. The dotted line is the classical ($S \to \infty$) result. Solid lines are the QMC [5] and the T-matrix results [6], respectively. Inset: slope function (see text) vs x [8]
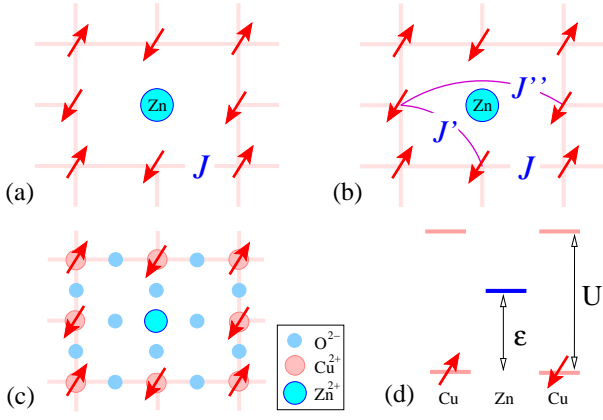
FIG. 2: (Color online) AF bonds in the (a) dilution-only model, (b) model with impurity-induced frustration (two out of six frustrating bonds are shown). (c) The CuO$_2$ plane with a Zn impurity. (d) Schematic local level diagram in the impurity-doped system.

to a reduction of M. However, since the order is suppressed already in the undoped system, this mechanism is unlikely to enhance fluctuations specifically due to dilution. Using an expansion of M in the dilution fraction x and in the extended interaction J_2, one obtains at small x and J_2:

$$ R(J_2) \approx R(0) \left(1 + A \frac{J_2}{J} \right), \quad (2) $$

where $A \lesssim 1$ [10] and $R(0)$ is the theory slope from Fig. 1. Thus, a large correction to the slope of the $M(x)/M(0)$ curve in the extended model is only possible if $J_2 \sim J$, which is beyond the realistic range in the cuprates where J_2/J is at most of the order of 10% [11]. A recent study [11] has shown that while extended interactions are important for explaining the lower *absolute* value of the staggered magnetization, they are not able to explain the large initial slope in the $M(x)/M(0)$ dependence. Thus, one must seek another explanation.

Extra interactions.—The dilution picture seems natural for modeling the replacement of a magnetic Cu site by a magnetically inert Zn; see Fig. 2(a). However, for the dilution-only picture to be valid, the Zn-site must remain *electronically* inert at energy scales up to the Hubbard U. Since it is the three-band Hubbard model that describes the real CuO$_2$ plane and other transition-metal oxides [12], the states on the oxygen orbitals also become important. They hybridize to Zn and remain involved in virtual hoppings between surrounding Cu-sites, see Fig. 2(c), facilitating extra superexchange couplings that connect further neighbor Cu-sites. Thus, the spinless impurity, in effect, leads to a cage of frustrating interactions around itself, with four J'_{Zn} and two J''_{Zn}; see Fig. 2(b). Qualitatively, the impurity-doped system is *not* equivalent to the site-diluted Hubbard model with electronically inert impurity sites, but rather to the t-ε-U model,

$$ H = -t \sum_{ij,\sigma} c^\dagger_{i,\sigma} c_{j,\sigma} + \varepsilon \sum_{l,\sigma} n^{Zn}_{l,\sigma} + U \sum_i n_{i,\uparrow} n_{j,\downarrow} , \quad (3) $$

a visual representation of which is given in Fig. 2(d). The

t-U part is the usual Hubbard model, which at half-filling reduces to the Heisenberg model at t^2/U order. The higher-order terms are negligible ($\sim t^4/U^3$) if $t \ll U$. The distinct physics is brought into play by the model (3) when the energy cost at the impurity site ε is less than the Hubbard gap. In that case, virtual transitions through the impurity level will cause superexchange interactions of order of $\sim t^4/\varepsilon^3$. Taking $\varepsilon = U/2$ and $U/t = 10$ for an estimate leads to $J'_{Zn}/J \sim (t/U)^2(U/\varepsilon)^3 \sim 0.1$. The total impact of the impurity-induced frustrating interactions per impurity is then $J'_{tot} = 4J'_{Zn} + 2J''_{Zn} \sim 0.6J$, which, as we will show below, is enough to explain the discrepancy between dilution-only theory and experiments. As is discussed above, the corresponding Hubbard terms of the 4th order are smaller and do not disturb the order parameter specifically due to dilution.

For the realistic values of the CuO$_2$ plane parameters, mapping of the three-band Hubbard model to the single-band one can be done using the cell-perturbation approach [13] which does not require the smallness of the Cu-O hopping t_{pd} with respect to the charge-transfer gap Δ [14]. In this approach, locally hybridized states on Cu and surrounding O's are diagonalized exactly and the three-band model becomes a "multi-orbital" Hubbard model with the effective "Cu" states connected by effective hoppings. Since the lowest states in the multi-orbital Hubbard model are the same as in the single-band one (*i.e.* the lowest two-hole state is the Zhang-Rice-like singlet) the equivalence of the two models can be justified [13]. In this approach, even if Zn is inert electronically, the remaining O-like states in the Zn-O$_4$ cluster can facilitate couplings between neighboring Cu spins, Fig. 2(c).

We extend this approach to the Zn-doped case and perform a detailed microscopic calculations of J'_{Zn} and J''_{Zn} [15]. First, we fix the parameters of the three-band model so they yield the experimental value of the Cu-Cu superexchange $J \simeq 0.13$eV [13]. Since the electronic parameters of Zn states are not known precisely [16, 17], we vary them substantially as shown in Fig. 3 for a representative set of the three-band model parameters. Our Figs. 3(a),(b) show how the energy ε_{Zn} of the lowest effective "Zn" state depends on the energy of the bare Zn-level, Δ_{Zn}, and the hybridization, t_{Zn-O}, respectively. The effective Hubbard energy U_{eff} is also shown to demonstrate the validity of the qualitative level structure in Fig. 2(d) and to support our model (3). Figs. 3(a),(b) show that the electronic levels of Zn and hybridization with them are important in lowering ε_{Zn} and enhancing J'_{Zn} and J''_{Zn}.

Our Figs. 3(c),(d) show the Δ_{Zn} and t_{Zn-O} dependence of the total impurity-induced frustrating interactions per impurity J'_{tot}/J. Given the uncertainty in Δ_{Zn} (from 2-3eV, [16], to 5eV, [17]), the total frustrating effect can be estimated to be between $J'_{tot} \sim (0.2 - 1.0)J$. Individual J'_{Zn} and J''_{Zn} are in the range of 3-15% of J. Counterintuitively, the interaction across the impurity (J''_{Zn}) is greater than the next-nearest neighbor interaction (J'_{Zn}) due to partial cancellation of the super-exchange and the ring-like exchange involving Zn and three Cu sites on a nearest-neighbor plaquette, see Fig. 2(b). This results in a *stronger* bond between copper spins across
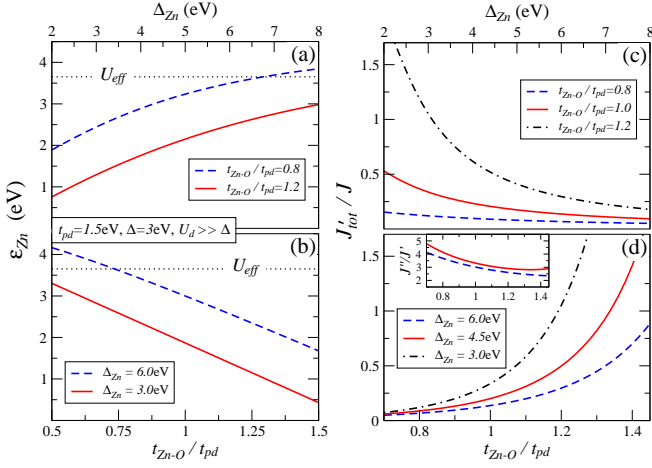
FIG. 3: (Color online) (a) and (b): energy ε_{Zn} of the lowest state on the effective "Zn"-site (ZnO$_4$ cluster) vs Δ_{Zn} and t_{Zn-O}, respectively. (c) and (d): $J'_{tot} = 4J'_{Zn} + 2J''_{Zn}$ vs Δ_{Zn} (for several values of t_{Zn-O}) and t_{Zn-O} (for several values of Δ_{Zn}), respectively. Inset (d): J''_{Zn}/J'_{Zn} vs t_{Zn-O}. In (a-d), $t_{pd} = 1.5$eV, $\Delta = 3$eV, $U_d \gg \Delta$.

the Zn-site, with the ratio $J''_{Zn}/J'_{Zn} \simeq 2 \sim 4$ in a wide range of the three-band model parameters, see inset in Fig. 3(d). Altogether, the three-band model provides support to our idea and gives an order-of-magnitude estimate of the parameters.

Low-energy model.—With this microscopic insight, one should model the Zn-doped CuO$_2$ plane by the Heisenberg model with random impurities not only causing more fluctuations by cutting links [3], but also connecting the nearby spins in a frustrated way. Thus, the effective model is:

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J'_{Zn} \sum_{\langle ij \rangle'} \mathbf{S}_i \cdot \mathbf{S}_j + J''_{Zn} \sum_{\langle ij \rangle''} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4)$$

where the first term is the dilution-only model with $S = 1/2$ spins for all the sites except the impurity sites (where $S = 0$) and the sums over the J'_{Zn} and J''_{Zn} bonds are taken around the impurity sites only, as shown in Fig. 2(b).

Suppression of the order parameter.—We have investigated the model (4) by means of the analytical T-matrix as well as unbiased QMC techniques. The former is based on the diagrammatic treatment of the corresponding linear spin-wave theory with exact calculation of the scattering amplitudes off the impurities and subsequent disorder averaging. The details of the approach for the dilution-only problem are given in Ref. 6 and results for $M(x)/M(0)$ are shown in Fig. 1. The modification of this method for the model (4) concerns changes in the p- and d-wave scatterings off the impurities, while the s-wave contribution can be shown to be unaffected by the frustrating terms [15]. The advantage of this method is that both the x- and J'_{Zn}, J''_{Zn}-dependence of the order parameter can be studied systematically.

QMC simulations were performed using the stochastic series expansion method [18] to find the staggered magnetiza-

tion in lattices with $N = L \times L$ sites:

$$M_L^2 = \frac{3}{N^2} \left\langle \left(\sum_i (-1)^{x_i + y_i} S_i^z \right)^2 \right\rangle. \quad (5)$$

The frustrating interactions generally present a serious difficulty due to the negative sign problem [19], which becomes more serious (exponentially) with increasing number of frustrating bonds and inverse temperature $\beta = J/T$. Here we focus on the system with a single impurity, where the sign problem is completely local (independent of the lattice size) and, in the range of frustration of interest here, manageable down to sufficiently low temperatures to draw conclusions about ground states of relatively large lattices. For all lattices considered below, M_L is well converged already at $\beta = 16$, and in the following we use this value. We assume the usual size-dependence of the staggered magnetization [20, 21]:

$$M_L^2 = M^2 + \frac{m_1}{L} + \frac{m_2}{L^2} + \frac{m_3}{L^3} + \ldots, \quad (6)$$

As a check, we calculated M for a pure AF using the same system sizes and $\beta = 16$, which gave $M \approx 0.3066$ for the extrapolated value, only slightly below high-precision result obtained using much larger lattices; $M = 0.30743(1)$ [22].

We are interested in the suppression of $M(x)$ at low impurity concentrations; $M(x)/M(0) \approx 1 - xR(0)$, where $R(0)$ is the slope of the M vs x curve at $x \to 0$. We introduce a finite-size analog of the slope function as

$$R_L = \frac{1}{x} \left[1 - \frac{M_L(1)}{M_L(0)} \cdot \frac{1}{1-x} \right], \quad (7)$$

where L is the lattice size, $M_L(1)$ is the staggered magnetization of the system doped by one impurity, and $x = 1/L^2$ for that case. The normalization by $(1-x)$ is necessary to convert M found from (5) to weighting M relative to the amount of magnetic sites [8]. Fig. 4(a) shows the size dependence of the slope in both the unfrustrated J-only model and the frustrated model with $J''_{Zn} = 2J'_{Zn} = 0.07J$ and $0.1J$. The latter set is still below the frustration beyond which the sign problem becomes too serious. As expected, the frustration increases the slope substantially. Given the non-linearity of the data, there is some uncertainty in the $1/L \to 0$ extrapolation. We here use a linear fit to $L \geq 8$ data; see Fig. 4(a). Due to some remaining nonlinearities (which are seen clearly for sizes $L < 8$), the extrapolation may slightly under-estimate the slope $R(0)$, and should therefore be considered a lower bound.

To obtain a direct quantitative measure of the effect of frustration we consider the difference $\Delta R_L = R_L^f - R_L^0$ of the slopes from (7) for the model (4) with (R^f) and without (R^0) frustrating terms, respectively, for lattice sizes L and several J'_{Zn} and J''_{Zn}. We perform finite-size extrapolations to the thermodynamic limit as above for each set of couplings; examples are shown in the inset of Fig. 4(a). An unexpected finding is that two J''_{Zn} bonds suppress the order at almost the same rate as four J'_{Zn} bonds of the same strength, as evidenced by both the QMC and the T-matrix results. Combining that with the systematically larger values of J''_{Zn} from
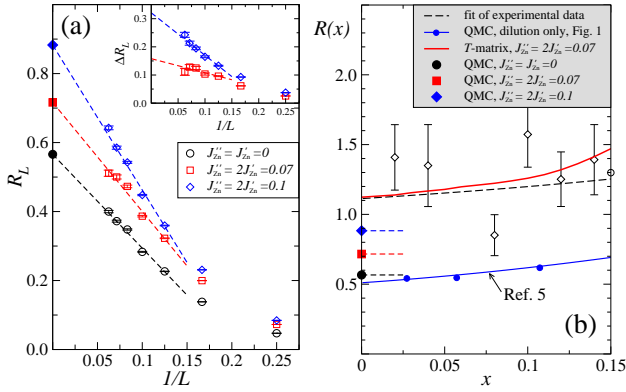
FIG. 4: (Color online) (a) The slope R_L, Eq. (7) vs $1/L$ in systems with and without frustration ($\beta = 16$), solid symbols are extrapolated values. Inset: slope increase ΔR_L due to frustration. (b) Same as inset in Fig. 1 with the T-matrix results for $J''_{Zn} = 2J'_{Zn} = 0.07J$ and QMC extrapolations of $R(0)$ from Fig. 4(a) for $J''_{Zn} = 2J'_{Zn} = 0$, $0.07J$, and $0.1J$. QMC data provide lower bounds of the slopes.

the three-band model calculations shows that this interaction is particularly important.

Fig. 4(b) shows that the experimental slope $R(0) \approx 1.1$ is matched by the T-matrix results already at $J''_{Zn} = 2J'_{Zn} = 0.07J$ ($J'_{tot} = 0.28J$) where we fixed the ratio to 2 according to the three-band model results. QMC results from Fig. 4(a), extrapolated to $x \to 0$, are shown in Fig. 4(b) for the same and larger values of frustration, $J''_{Zn} = 2J'_{Zn} = 0.1J$ ($J'_{tot} = 0.4J$). They yield the lower bounds for the slopes $R(0) \approx 0.7$ and 0.9, respectively [23]. The results suggest that a stronger frustration, close to the latter data set or somewhat larger, is present in the real Zn-doped CuO_2 plane. This is still a reasonably modest amount of frustration, well within the window suggested by the three-band model calculations.

Using the same QMC analysis, we have also investigated an alternative mechanism of the enhanced order suppression by impurities, in which the strength of the J bonds in the vicinity of Zn is reduced by the lattice distortion [24]. We found that changing the bond strength by 15% ($\delta\widetilde{J}_{tot} = 1.2J$) changes the slope R(0) by at most a few percent, ruling out the lattice-distortion mechanism of the order suppression as a viable alternative to our theory.

Conclusions.—We have proposed that impurity-doped strongly correlated systems develop significant frustrating interactions, which are absent or negligible in the corresponding undoped system, due to electronic degrees of freedom at the scale less than the Hubbard-U. Applying this mechanism to the problem of the doped non-frustrated Heisenberg model, relevant to Zn-doped cuprates, we have found this effect to be the key to resolving discrepancies between experiments and earlier theories. Our analytical and numerical results agree well with each other. We estimate the total amount of frustration to be $\gtrsim 0.4J$ per impurity in the Zn-doped CuO_2 plane. In light of our quantitative theoretical results, further high-precision experiments at low doping are called for.

Outlook.–Our theory has far-reaching consequences for di-

luted AFs and other doped Mott insulators. The character of the percolation transition should change as a result of the frustrating interactions across the impurities. The impurity-doping of spin chains should introduce weaker links between the broken pieces. Recent experiments on doped frustrated J_1-J_2 systems [25] should be affected by the same mechanism. The proposed impurity-induced frustrating interactions should persist at the finite doping and may produce a pair-breaking mechanism in the doped CuO_2 planes.

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[23] Using the data from the four largest clusters only, linear extrapolation for the $J''_{Zn} = 2J'_{Zn} = 0.1J$ data set in Fig. 3(b) gives $R(0) \approx 1.0$, much closer to the desired value.

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